Recent progress in thin film organic photodiodes

Inganäs, Olle; Roman, Lucimara S.; Zhang, Fengling; Johansson, D.M.; Andersson, M.R.; Hummelen, J.C.

Published in:
Synthetic Metals

DOI:
10.1016/S0379-6779(00)01448-X

Publication date:
2001

ELSEVIER

Synthetic Metals 121 (2001) 1525–1528

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Recent progress in thin film organic photodiodes

Olle Inganäs[a*], Lucimara S.Roman[a], Fengling Zhang[a], D.M. Johansson[b], M. R. Andersson[b], J. C. Hummelen[c]

[a]*Dept Physics Linköping University, S-581 83 Linköping, Sweden*
[b]*Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden,*
[c]*Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Abstract

We review current developments in organic photodiodes, with special reference to multilayer thin film optics, and modeling of organic donor -acceptor photodiodes. We indicate possibilities to enhance light absorption in devices by nanopatterning as well as by blending, and also discuss materials science issues of nanostructure in blends and in vertically stratified multilayer devices. Our current best devices have external efficiencies of 30-50% in between 400-600 nm, and show fill factors of 0.54 illuminated under weak monochromatic light.

Keywords: Photodiodes, Polymer, Fullerene

Introduction

The use of thin organic films for photoelectric energy conversion and for photodiodes is receiving increasing interest. The combination of donor and acceptor in blends [1-3] is a dominant theme. While efficient and stable photovoltaic devices look far on the horizon, the quickening of the pace of development is quite dramatic. This is much due to the efforts of synthetic chemists in preparing new organic polymers and molecules, among which photoinduced charge transfer and subsequent charge collection basically defines the device function. New aspects may also be derived from the field of physics, optics and materials science, to contribute to the development of better performing devices, and to handle some of the problems not easily solved by chemical design. In this paper, we review some recent developments and describe state of the art devices based on the principle of vertically stratified photovoltaic devices.

Optical modelling and optimization of bilayer devices

The creation of photoexcitations in conjugated polymers and molecules occurs through absorption; therefore the act of absorption is the primary act of photovoltaic conversion and sets the scene for coming events. We have modeled the optical absorption features on thin organic films and devices, using spectroscopic ellipsometry to define the full dielectric function (in the visible and near infrared range) for the different organic molecules and polymers used in our devices [4-5]. The devices are normally thinner than a few wavelengths of light. Given the wavelength dependent optical constants, and the thickness of each layer, we can easily build a full optical model for the operation of bilayer (or multilayer) devices, using transfer matrix techniques[4]. Such modeling allows us to tune the geometry/thickness in order to locate the monochromatic standing waves within the thin film devices. The location of the maximum of the optical electrical field may therefore be chosen by considering the thickness; as absorption events cause the photocurrent, we would therefore prefer to maximize the

* Corresponding author. Tel: +46-13-28 12 31; fax: +46-13-28 89 69;
E-mail: ois@ifm.liu.se

PII: S0379-6779(00)01448-X

optical electrical field at places where rapid excitation dissociation and collection occurs. This may be found at the interface between a conjugated polymer and C_{60} in polymer/C_{60} devices. This purely optical effect goes a long way towards explaining the spectral dependence of photocurrent in these devices, when exciton diffusion is used to model the photocurrent generation [4]. This model can also be used, with proper modifications, to predict the amount of photoluminescence quenching in polymer /C60 bilayers [6].

Electrical aspects of transport in polymer/ C_{60} bilayer photodiodes

The optical model does not account for the voltage dependence of photocurrent, however, and studies of the electrical transport in polymer/ C_{60} devices in the dark indicate that most of the voltage drop in the device is found within the C_{60} layer. This low mobility layer is operated under high field conditions, where space charge limitations are observed; this allows us to extract a value of charge carrier mobility at least one order of magnitude lower than that found in the polymer layer. It is therefore difficult to optimize the thickness of the C_{60} layer purely from optical considerations; the transport of photogenerated electrons is severely compromised by this approach.

From these studies it is clear that the conductivity and mobility of the C_{60} layer is crucial, and that it may cause intrinsic limitations to the transport of photocurrent. A simplistic estimate may establish an approximation; with a photocurrent density of 10 mA/cm^2, a C_{60} layer thickness of 35 nm, a ohmic voltage drop of 0.1 V through the layer requires a conductivity of 3.5×10^{-7} S/cm. This is close to various experimental determinations of the transport properties of the material, as prepared by vacuum evaporation. Indeed, it is reported [7] that the electron mobility of polycrystalline C_{60} is strongly influenced by oxygen, dropping from 1 cm^2/Vs to values close to 10^{-5} cm^2/Vs, within an order of magnitude of the mobilities obtained in our studies, where the C_{60} is exposed to atmosphere. We expect all the derivatives of C_{60}, often used in polymer blend photovoltaic devices, to show somewhat lower mobility than pure C_{60}, due to increased distance between the fullerene in the solid phase. Even more decreased is the expected mobility for C_{60} dispersed in polymer matrices, as used in donor-acceptor distributed junctions [8].

We have found that vertical segregation of donor/acceptor layers, in order to prevent anode-cathode contact through one and the same polymer or molecule phase, enhances fill factor performance, photocurrent and photovoltage [9]. These vertically stratified photodiodes, where soluble acceptors are spincoated on top of a polymer layer, to form photodiodes with good performance, reach photocurrent densities of 1 mA/cm^2 and photovoltages of 0.8V under AM1.5 1 sun, while also giving good fill factors (0.5). Evidence here also points to bulk transport in the acceptor phase to be current limiting. We note that recent results [10] report higher photocurrent densities (≈5.2 mA/cm^2 under AM1.5 1 sun) than we extract in our devices. One of the experimental variations in these studies is the methods of preparation, which are done under exposure to atmosphere in our studies. The decrease of conductivity in C_{60} layers under atmosphere exposure (oxygen) can go beyond one order of magnitude [11], a decrease which may go some way towards explaining the lower photocurrents in our present devices.

Nanopatterning and polymer selfassembly - tools for enhanced optical input

Given the necessity to use thin films of materials, it is imperative to make the best use of the photons impinging on the film. Minimizing reflectance by choosing the thickness distribution in multilayer devices is a possible route towards this goal. The analysis of external and internal quantum efficiencies for photovoltaic devices is helpful in this regards [4-5], but requires a physically complete picture of the photocurrent generation mechanisms. Considering that electronic transport always seems to be limiting devices, it should be attractive to enhance the photon path in the photodiode, in order to enhance the total amount of optical absorption. By coupling the incoming light into waveguided modes within the thin organic layers, this goal should be reached. We have demonstrated that this method can be used to enhance photocurrents in polymer/derivatized C_{61} devices [12] where the organic layer has been topographically patterned with optical gratings, transferred with the help of soft lithography based on elastomer replicas. This method of nanopatterning is quite feasible also for large area nanopatterning, but optimization of devices will require a very detailed optical modeling.

The design of efficient photovoltaic devices also requires the extension of optical absorption towards lower energies. To use this part of the solar spectrum, where much of the energy is found, we need new polymers and organic molecules. We will normally not be able to use a single compound to cover all the energetically valuable part of the solar spectrum; therefore we need to use more than one material. It is indeed quite possible to use a collection of "antenna" polymers to collect energy from the solar spectrum, and then to transfer this energy by excitation transfer to polymers of lower bandgap; this mechanism can also be used to enhance photocurrents[13]. Control over the molecular miscibility is desirable in order to use this mechanism, which is an induced dipole-dipole interaction with short distance of action. The nanostructure of polymer blends has been shown to be crucial to the operation of polymer/ C_{60} blend devices[14].

New vertically stratified multilayered device

A recent extension of vertically stratified photovoltaic devices is found in the case of a novel high molecular form

of MEH-PPV combined with the derivatized C_{61} molecules PCBM (methanofullerene [6,6]-phenyl - C_{61}-butyric acid methyl ester)(15). Here we form a graded junction of PCBM on top of the MEH-PPV film. MEH-PPV is not dissolved in xylene unless heated above 90°C. Therefore the second layer spin-coating of PCBM in xylene at room temperature will not dissolve MEH-PPV. The PL of MEH-PPV was strongly quenched indicating that PCBM is present throughout the polymer layer. MEH-PPV was first deposited on a PEDOT-PSS layer on top of ITO. The thickness of MEH-PPV is 80-120nm and PCBM is 30-45nm. A 30nm Al layer was evaporated on top of PCBM as a cathode and the active area is ≈ 4 mm^2. The experimental setup is same as those in reference[9].

The layer thicknesses of the devices were changed by changing spin-coating rate. Three different thick diodes were made. The performances of these devices are very sensitive to the thickness of the active layer. The external quantum efficiency (EQE) changes with the layer thickness as shown in figure 1 for diodes 3, 2, 1 (increasing thickness of MEH-PPV and PCBM).

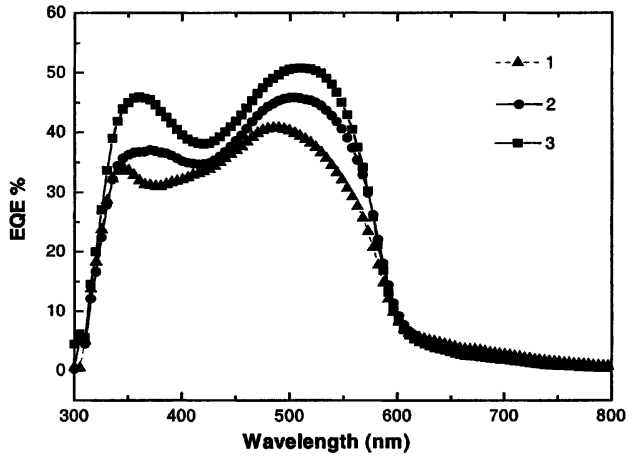

Fig. 1. The EQE of three bilayer devices (MEH-PPV/PCBM) with different thickness. The light source used was the tungsten-halogen lamp (Oriel). The maximum intensity is 0.21mW/cm^2 in range of 300-800nm.

The EQE were more than 30% between 400-600 nm in all three diodes, and reached 50% at 510nm and 10% even at 600nm in the thinnest diode 3. The I-V characteristics of these devices are presented in figure 2. The open circuit voltage increased, but short circuit current as well as EQE decreased with the increasing thickness of active layers in the diodes. V_{oc} are 560, 630, 650mV, I_{sc} are 28, 25, 19.9 μA/cm^2, respectively, for diodes 3, 2, 1 under illumination at λ=540nm with intensity 0.14mW/ cm^2. The rectification in the dark (-1.5V to 1.5V) is more than 5 order of magnitude and the fill factor (FF) is 0.54.

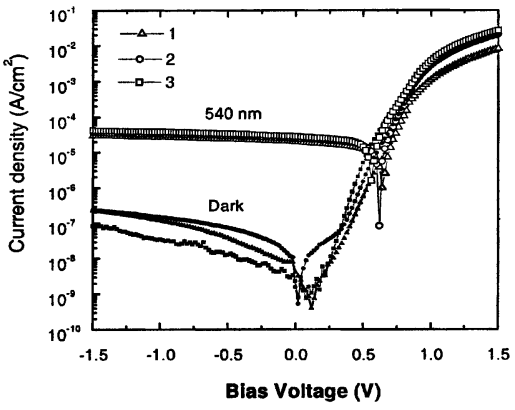

Fig. 2. The I-V characteristics of devices under dark and illuminated at λ=540nm with light intensity of 0.14mW/cm^2.

Similar performance was observed in the diode by using chloroform instead of xylene as solvent for MEH-PPV (see figure 3). All these performances are comparable with the data reported on first generation of vertically stratified photovoltaic devices.

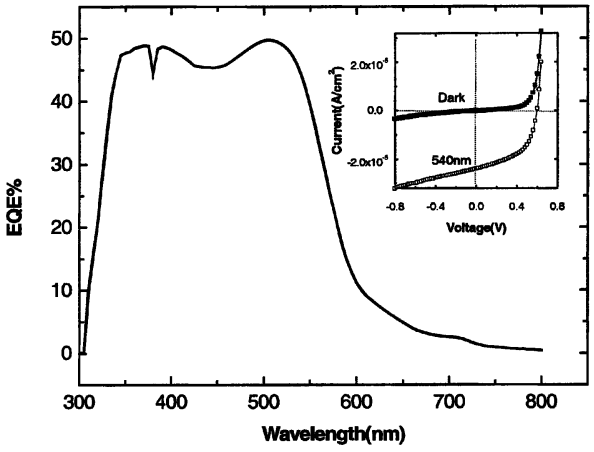

Fig. 3. The EQE of bi-layer devices made of MEH-PPV in chloroform and PCBM in xylene. The inset shows the I-V characteristics under dark and illuminated at λ=540nm.

When the diodes were illuminated by simulated solar light AM1.5 with the intensity of 78mW/ cm^2, the FF dropped abruptly in all three diodes. The FF dropped to 0.25 and ECE to 0.4% even in the best devices diode 3, although the V_{oc} increased to 0.79V and I_{sc} to 1.5mA/ cm^2. The I-V curves are shown in figure 4. There are clearly more than series resistance limiting the performance of the

devices, the shape of I-V curves indicated a more complex mechanism. Earlier generations of similar devices show more distinct series resistance limitations. Methods to enhance the conductivity and mobility of the acceptor layer may be necessary.

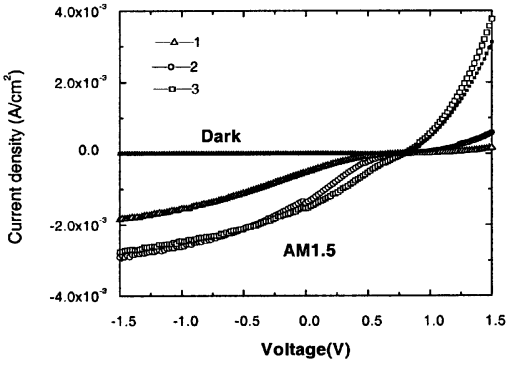

Fig. 4. The I-V curve of bilayer devices (MEH-PPV/PCBM) illuminated by simulated solar light AM1.5 with the intensity of 78mW/ cm^2.

Conclusions

Charge transport processes are suggested to be limiting the performance of organic thin film photodiodes prepared from conjugated polymers and molecular acceptors. The rapid rate of progress in the field may also come to relieve this limitation; meanwhile, several approaches (patterning, blending...) are possible to use in order to increase the optical input of energy into the thin film devices. The processability and solubility of polymers and organic molecules are crucial for generating such structures.

Acknowledgements

Work summarized here have been supported by the Göran Gustafsson Foundation, the Swedish Research Council for Engineering Sciences, the Swedish Research Council for Natural Sciences, the Swedish Foundation for Strategic Research, Carl Tryggers Foundation and the Joule III project JOR-3CT980206 (MOLPLASOL). Many students and postdocs have contributed, in particular Leif Pettersson, Lichun Chen, Mathias Theander, Mattias Svensson, ...

References

1. N.S. Sariciftci, L.Smilowitz , A.J. Heeger, F. Wudl, Science 258 (1992) 1474.
2. G.Yu, J.Gao, J.C.Hummelen, F.Wudl, A.J.Heeger, Science, 270 (1995) 1789.
3. J.J.M.Halls, C.A.Walsh, N.C.Greeham, E.A.Marseglia, R.H.Friend, S.C.Moratti, and A.B.Holmes, Nature 376 (1995) 498.
4. L.A.A.Pettersson, L.S.Roman, and O.Inganäs, J. Appl. Phys.86(1) (1999) 487.
5. L.S.Roman, W.Mammo, L.A.A.Pettersson, M.R.Andersson, and O.Inganäs, Adv. Mat. 10 (1998) 774.
6. M.Theander, A.Yartsev, D.Zigmantas, and V.Sundström, W.Mammo and M.R.Andersson, O.Inganäs, Phys. Rev. B, 61(19) (2000) 12957.
7. R.Könenkamp, G.Priebe and B.Pietzak, Phys.Rev. B 60 (1999) 11804.
8. C.J.Brabec, F.Padinger, N.S.Sariciftci,J.C.Hummelen, J. Appl. Phys.85 (1999) 6866.
9. L.C. Chen, D.Godovsky, O.Inganäs, J.C.Hummelen, R.A.J.Janssens, M.Svensson and M.R.Andersson, Adv. Mat. 12 (2000) 1367.
10. Brabec, these proceedings.
11. C. H. Lee, G. Yu, B. Kraabel, D. Moses , V. I. Srdanov Physical Review B 49 (1994) 10572.
12. L.S.Roman, O.Inganäs, T.Granlund, and T.Nyberg, M.Svensson, M. R.Andersson, and J.C.Hummelen, Adv. Mat. 12 (2000) 189.
13. L.Chen, L.S.Roman, M.D.Johansson, M.R.Andersson, R. A. J. Janssen and O.Inganäs, Adv.Mat 12 (2000) 1110.
14. L.S.Roman, M.R.Andersson, T.Yohannes, O.Inganäs, Adv. Mat. 9 (1997) 1164.
15. J. C. Hummelen, B. W. Knight, F. LePeq, F. Wuld, J. Yao, C. L. Wilkins, J. Org. Chem. 60 (1995).532.